

## Plastic Behavior of Coal Under Rapid-Heating High-Temperature Conditions

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### Introduction

Bituminous coals upon heating undergo a number of physical and chemical changes. The solid coal passes through a transient plastic (fluid) phase before it resolidifies to form coke. This transient fluidity results in caking and agglomeration of the coal particles in the processing of many bituminous coals. Industrially, these phenomena may contribute to desirable process performance such as a strong and reactive product in metallurgical coke manufacture, or to undesirable operating behavior such as bed bogging in fixed or fluidized bed gasifiers. More fundamentally, the presence of the fluid phase can influence the pyrolysis rate process. A basic understanding of the plastic behavior of coal is therefore essential in the development of quantitative understanding of modern coal conversion and combustion processes.

The mechanism of coal plasticity is poorly understood. One picture is that softening is initiated by a superposition of physical melting and pyrolysis of the coal. A plasticizing agent (metaplast) generated by these processes maintains fluidity until evaporation, repolymerization, and thermal cracking reduce its concentration to a subcritical value causing resolidification (1-3). Previous studies of coal plasticity have mainly been performed under conditions pertinent to metallurgical coke making; i.e., low heating rate carbonization of packed bed samples. A standard instrument is the Gieseler plastometer which operates at a heating rate of  $5 \times 10^{-2} \text{ K s}^{-1}$  to final temperatures around 800 K. Plasticity data are needed at the high heating rates and temperatures (up to  $15,000 \text{ K s}^{-1}$  and 700 - 1300 K, respectively), and elevated hydrogen pressures (up to 10 MPa) of interest in coal conversion.

A new apparatus (4) has been developed that allows the rapidly changing plasticity of softening coal to be measured as a function of the following operating conditions, each varied independently over the stated range: heating rates 40 -  $800 \text{ K s}^{-1}$ , temperatures 600 - 1250 K, particle diameters less than 100  $\mu\text{m}$  and pressures of inert or reactive gases from vacuum to 10 MPa. This paper presents the findings of a detailed study of the plasticity of a high volatile Pittsburgh No. 8 seam bituminous coal using this instrument. Typical results are presented and compared to predictions of a preliminary mathematical model of coal plasticity. The inventory of fusible material within the coal was independently determined by pyridine extraction of rapidly quenched flash-pyrolyzed chars and correlated with the plastic behavior. The effect of the time-temperature history of the coal on the molecular weight of this extract was determined by gel permeation chromatography.

### Experimental

#### (a) Plastometer

The plastometer is described in detail elsewhere (4). Briefly, the technique involves measuring the torque required to rotate at constant speed, a thin shearing disk embedded in a thin layer of coal initially packed as fine particles, and confined between two heated metal plates. The unit is enclosed in a high-pressure vessel that can be evacuated or charged with hydrogen or inert gas. One end of the torque transducer is joined to the shaft of the shearing disk, while the other end is driven by a gear motor. Response time of the piezoelectric transducer is less than 10 ms.

The details of the coal shearing device are illustrated in Figure 1. The shearing chamber consists of a 0.50 mm thick shearing disk of 3.75 mm radius in a 38.1 mm x 0.76 mm slot formed by upper and lower bounding plates held together by a pair of stainless steel/ceramic clamps. The thin coal layer between the disk and each bounding plate is thus 0.13 mm (or about two particle diameters for the size of particles tested). The shearing disk and bounding plates are machined from a nickel superalloy for high-temperature strength, corrosion resistance, and high electrical resistivity. Measurement of temperature is by a thin-foil thermocouple of 0.013 mm thickness (response time 2 - 5 ms) attached to the outside surface of the upper metal plate of the shearing chamber. Heating is by sequentially passing two constant pulses of current of pre-selected magnitude and duration through the metal plates for heating up and holding the sample temperature, respectively. Currents as high as a few hundred A are drawn from the 12 volt DC source for sample heatup. A loading device (not shown here) (4) is used to permit reproducible loading of the coal particles into the shearing chamber and alignment of the rotating disk with the axis of the transducer shaft. The assembled and loaded shearing chamber is placed between the two electrodes in the viscometer before the experiment, and the couplings to the transducer are then connected. To protect the transducer against overload during startup, the shearing disk is rotated manually one or two turns until a torque in a measurable range of  $4 - 5 \times 10^{-2}$  Nm is attained. The unit is then evacuated to approximately 5 Pa and flushed twice with helium at 0.1 MPa. Then the test gas is admitted until the desired test pressure is established. The drive motor is started 0.5 s before the heating circuits are activated. The torque vs time, and temperature vs time profiles throughout the entire run are each recorded on an electronic recorder at a rate of 200 points/s, digitized, and stored for subsequent data processing.

#### (b) Screen Heater Reactor

The weight loss and extract yield data are obtained from an enlarged and modified version of the screen heater reactor described by Anthony (5). Coal particles (~30 mg) of the same size used in the plastometer study (63 - 75  $\mu$ m) are spread in a thin layer between two faces of 425 mesh stainless screen of 14 cm x 7 cm size. The screen is mounted between two electrode blocks and heated by the same high-current circuits used for the plastometer. One of the electrodes is spring-loaded so that the screen is held tight throughout the entire run. Volatiles readily escape the immediate neighborhood of the screen and are diluted by the ambient reactor gas (usually helium). At the end of the preset heating interval, a cooling valve is automatically activated, and sprays pressurized liquid nitrogen onto the screen, resulting in a substrate quenching rate exceeding  $1100 \text{ K s}^{-1}$ . The weight loss of coal is determined by weighing the loaded screen before and after the run. The extract yield is then determined by Soxhlet extracting the screen and char with pyridine, drying the extracted screen and char in a vacuum oven at 120°C for 4 hours, and reweighing.

### Results and Discussion

The objectives of this work are to determine the separate effects of temperature, heating rate, pressure, reactive gaseous atmosphere, inorganic additives and pretreatment on coal plastic behavior and to formulate kinetic models for coal plasticity. Experiments to date have employed a Pittsburgh seam bituminous coal of 39% volatile matter and 63-75  $\mu$ m particle diameter. The coal, which was from the same mine as the samples used previously in this laboratory, was freshly ground under nitrogen, washed, sieved and then vacuum dried at 383 K for 4 hours.

#### (a) Typical Plastometer Results

Figures 2 and 3 present typical data obtained under 0.1 MPa and 3.5 MPa of helium, respectively, at a disk rotational speed of 0.67 rpm (corresponding to an average shear

rate of  $1.32 \text{ s}^{-1}$ ). In Fig. 2 the sample was heated at  $461 \text{ K s}^{-1}$  to a final temperature of  $874 \text{ K}$  and then held at this temperature for  $6.0 \text{ s}$ . As the temperature increases, the torque decreases to a low value due to liquid formation. After a period of low viscosity, the viscosity of the molten coal rises to a high value due to progressive resolidification of the melt. However, continued rotation of the disk breaks up the resultant coke formed by resolidification, and the torque vs time curve gradually decreases thereafter.

The stages of physical change of the coal are illustrated in Fig. 3. For the given shear rate, the torque is related to the absolute viscosity by  $1.0 \times 10^{-2} \text{ Nm} \equiv 2.6 \times 10^4 \text{ Pa s}$ , obtained by calibrating the instrument with viscous liquid standards at room temperature using a method described elsewhere (4). Essentially, the shearing geometry is regarded as two sets of concentric parallel disks. A calibration factor is introduced to account for the slight deviation of the actual instrument geometry from the parallel disk geometry. The apparent Newtonian viscosity is then obtained using the standard equation for a concentric rotating disk viscometer and the calibration factor.

To show how different types of particles behave when heated in the plastometer, samples of Montana lignite (dried,  $53\text{--}88 \mu\text{m}$ ), quartz ( $<106 \mu\text{m}$ ), Pittsburgh No. 8 coal (dried,  $63\text{--}75 \mu\text{m}$ ) and the same Pittsburgh coal pre-extracted with pyridine (dried,  $63\text{--}75 \mu\text{m}$ ) were separately tested. Fig. 4 compares these results. In the case of quartz, which does not change its physical form when heated, there is an initial drop in torque due to the slight thermal expansion of the shearing chamber when heated. A high but fluctuating torque signal reflects shearing of particles with rigid edges. Montana lignite, which undergoes pyrolysis without softening under these conditions, retains its solid form but experiences a decrease in volume due to weight loss. Its torque curve thus shows a gentle decrease to a steady value. The Pittsburgh coal shows a plastic behavior very different from the above solids. A low minimum torque value and a distinct plastic period are clearly present. Finally, the pyridine pre-extracted coal shows a delayed softening. Resolidification is faster and the plastic interval is shorter as compared with the untreated coal, presumably due to the prior removal of some metaplast precursor by pyridine.

#### (b) Typical Screen Heater Results

Information on the time-resolved kinetics of devolatilization, the amount of extractables formed within the coal and on the molecular weight distribution and chemical makeup of these extracts provides independent but complementary information about the mechanism of plasticity. Fig. 5 is a time resolved plot of yields of volatiles (i.e. weight loss), pyridine extractables from char, and the pyridine insoluble material in the char, for a heating rate of  $448 \text{ K s}^{-1}$  to a holding temperature of  $858 \text{ K}$ . After different holding times, the sample is rapidly quenched with liquid nitrogen (dotted line). The weight average molecular weight  $M_w$  of the extract is determined by a Waters Associates ALC/GPC 201 system using two series-connected  $100 \text{ \AA}$  and  $500 \text{ \AA}$  Microstyragel columns. Fig. 6 is a similar plot for a higher holding temperature. The quantity  $M_w$  is found to increase in both cases. Pre-extraction of the coal removes part of the liquid precursor, and less extract would be expected upon subsequent pyrolysis as was observed. This behavior can significantly affect the plastic behavior of coal. Fig. 7 compares the yields of pyrolysis-derived extracts from raw coal samples with those from pyridine pre-extracted samples, subjected to identical temperature-time histories. A second set of comparisons, for a different heating history, are also shown.

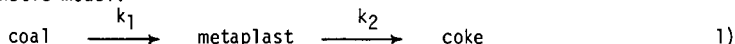
#### (c) Discussion of Results

The mechanism of plasticity in coals is not well understood for rapid heating and high temperature conditions. Plasticity and related phenomena such as swelling

and agglomeration are direct consequences of liquid formation by heating. Physical melting of part of the coal first occurs when the temperature is sufficiently high. Subsequent pyrolytic bond breaking generates additional liquid. The initial liquid generated by physical melting may also dissolve part of the solid coal material. At the same time, liquid is lost through evaporation of its lighter molecules (volatiles) from the particle, and through repolymerization and cracking reactions. This picture is supported by our present data. The kinetics of extract generation and destruction as inferred from the screen heater experiments correlates well with the plasticity data, as shown in Fig. 8. It seems reasonable to assume that the amount of extract is an indication of the instantaneous liquid metaplast content of the coal. Initially, we can extract 27% of pyridine solubles from the unheated raw coal. This amount would correspond to the material that is solid at low temperature but undergoes physical melting as temperature exceeds the 'melting' point. Our observation with the plastometer, that initial softening occurs around 580 K independent of heating rate ( $50 - 700 \text{ K s}^{-1}$ ), is consistent with the above observation as seen from Fig. 9. If this initial 27% of material is pre-extracted, and afterwards the coal is subjected to pyrolysis, the metaplast (extract) formed by pyrolysis alone is much less as seen from Fig. 7. The pre-extracted coal is expected to soften at a later time (higher temperature) and the duration of plasticity is shorter, as is observed (Fig. 4d).

The relation of extract inventory to the duration of plasticity and to resolidification rate is illustrated from the pyridine insoluble curves in Figs. 5 and 6. The amount of insolubles reaches a minimum and then rises to an asymptotic value determined by the competition of devolatilization and resolidification rates. The rising portion of the curves indicates either repolymerization reaction or cracking of metaplast to a light gas and a solid, or both. Repolymerization seems likely since the molecular weight of the metaplast increases with heating time (Figs. 5, 6). However, this can also be caused by selective evaporation of light molecules from the metaplast. The devolatilization rate also seems to be proportional to the instantaneous amount of metaplast in coal. At higher holding temperatures ( $\geq 973 \text{ K}$  for heating rates around  $500 \text{ K s}^{-1}$ ) the plasticity and extract curves do not correlate well. The extract curve has shorter width than the plasticity curve. This behavior may in part reflect an apparatus artifact since the mass transfer resistance for volatiles escape in the plastometer is much greater than in the screen heater.

The duration of plasticity and the resolidification rate are quite sensitive to temperature-time history (Figs. 9, 10). Fig. 10 shows how these vary for plastometer runs at  $450 \text{ K s}^{-1}$  to four different holding temperatures. This behavior leads to the conceptually simple mathematical model based in part on Fitzgerald's metaplast theory (6). He considered the formation and destruction of metaplast to be described by a first order kinetic model.



To simplify its implementation here, equivalent component densities and negligible weight loss are assumed. To relate metaplast concentration to the apparent viscosity of the melt, an expression for concentrated suspensions by Frankel and Acrivos (7) is employed. The relative viscosity  $\mu$  of a suspension at high solids concentration is given by,

$$\mu = \frac{\mu^*}{\mu} = \frac{9}{8} \left[ \frac{(\phi/\phi_m)^{1/3}}{1 - (\phi/\phi_m)^{1/3}} \right] \quad (2)$$

where  $\mu^*$  is the viscosity of a suspension with a solids volume fraction  $\phi$ ,  $\phi_m$  being the maximum value of  $\phi$  possible, and  $\mu$  is the viscosity of the continuous (solids-free) phase. We approximate  $\phi = 1 - M$  where  $M$  is the metaplast weight fraction. Since the sample is initially a packed bed of solids,  $\phi_m$  is assumed to be unity. This condition is possible if the solid elements of the suspension are thin slabs

(lamellae) which is a reasonable representation of the layered structure of vitrinite. Solving Equation 1 for metaplast concentration with the given temperature profile (constant linear heating followed by a constant holding temperature) and using Equation 2 allows  $\bar{\mu}$  to be calculated if the rate constants  $k_1$  ( $=k_{01} \exp[-E_{A1}/RT]$ ) and  $k_2$  ( $k_{02} \exp[-E_{A2}/RT]$ ) are known. These quantities can be estimated from laboratory data. At a late stage of resolidification, the metaplast formation rate is very small, so

$$\frac{dM}{dt} = -k_2 M \quad (3)$$

At small values of  $M$  ( $M < 0.1$ ), Equation 2 with the approximation  $\phi_m = 1.0$  is reduced to

$$\bar{\mu} = \frac{27}{8} \left( \frac{1}{M} \right) \quad (4)$$

It then follows that

$$\frac{d \ln \bar{\mu}}{dt} = k_2 = k_{02} \exp[-E_{A2}/RT] \quad (5)$$

The holding temperature is a good approximation for  $T$  when resolidification occurs well after the holding temperature is reached (such as in Fig. 2). The experimental rate of increase of the logarithm of torque is identical to the left-hand term of Equation 5. A plot of the logarithm of this quantity vs reciprocal holding temperature gives a straight line corresponding to an activation energy  $E_{A2}$  of  $133 \text{ kJ mole}^{-1}$  and  $k_{02}$  of  $2.0 \times 10^8 \text{ s}^{-1}$ . Actual viscosities are measured in the range  $1 \times 10^3 -$

$1 \times 10^5 \text{ Pa s}$ . Nazem (8) measured the viscosities of carbonaceous mesophase pitch at around  $623 \text{ K}$  and found them to be between  $30 - 200 \text{ Pa s}$ . Hence  $\bar{\mu}$  would be of order  $10 - 1,000$  if we assume the solids free metaplast has a similar viscosity. For illustration purpose,  $\mu$  is taken to be  $120 \text{ Pa s}$ . Values of  $k_{01} = 245 \text{ s}^{-1}$  and  $E_{A1} = 40.7 \text{ kJ mole}^{-1}$  are found to fit the plastic period of the experiments at  $450 \text{ K s}^{-1}$  heating rate (4). The temperature dependence of viscosity of the solids-free metaplast is not considered here. Calculated plasticity curve in Fig. 11 shows the same form of dependence of viscosity on reaction time as the observed data in Fig. 10. Fig. 12 shows that the calculated plastic period (smooth curve), defined as the time interval when  $\mu^* < 3.6 \times 10^4 \text{ Pa s}$ , fits the laboratory data well.

The above model is of preliminary nature and offers opportunities for improvement. Weight loss has not been considered in defining metaplast concentration. Generation of metaplast is described only by a first order chemical reaction, i.e. physical melting is neglected. This seems particularly suspect since curve fitting the present data with this model gave a low value of  $E_{A1}$  more suggestive, in the present context, of kinetics dominated by physical transport or phase change. Further, Equation 2 relating metaplast concentration to relative viscosity was derived for the highly simplistic case of solid spheres.

The plastic behavior under vacuum and high inert gas pressure was also investigated. For both vacuum and  $3.5 \text{ MPa}$  ambient helium pressure, the plastic period is shorter ( $4.5$  and  $4.2 \text{ s}$  respectively, compared to  $6.4 \text{ s}$  at  $0.1 \text{ MPa}$  helium pressure). The resolidification rates for both cases are faster than under  $0.1 \text{ MPa}$  helium. Under vacuum, the metaplast may escape faster from the particle, resulting in shorter plasticity duration. High pressure may favor repolymerization reactions, hence the resolidification rate. The effect of high pressure on fluidity agrees with inferences by Halchuk et al. (9) based on analyses of char particles from screen heater pyrolysis. They found that the fluidity of a HVA Pittsburgh No. 9 seam coal during rapid pyrolysis at  $760^\circ\text{C}$  was lower at pressures above  $0.45 \text{ MPa}$ , than that at  $0.1 \text{ MPa}$ .

## Conclusions

A new plastometer for measuring the apparent viscosity of plastic coals under rapid-heating, high temperature conditions has been developed and found to give reproducible data that are generally consistent with expected plasticity behavior. Under rapid heating conditions ( $40 - 800 \text{ K s}^{-1}$ ) the duration of plasticity and its rate of disappearance for a Pittsburgh No. 8 bituminous coal depended strongly on pressure, temperature, and heating rate. However, the initial softening temperature was insensitive to heating rate. Pre-extraction of the coal with pyridine at 389 K, typically yielded 25 - 30 wt% organic matter and strongly retarded plasticity on subsequent heating by delaying its onset and shortening its duration.

The effects of temperature on the duration of plasticity were correlated by a preliminary mathematical model relating viscosity of solid-liquid suspensions to the transient concentration of a plasticizing agent generated and depleted by single first-order chemical reactions in series. This simple kinetic picture is also in qualitative accord with the other observations described above. However, quantitative prediction of metaplast molecular weights, effects of pressure and particle size on plasticity, and of softening temperatures will require that transport processes and physical melting be included in the modelling. More detailed modelling will also be needed to describe other softening related phenomena, such as swelling and agglomeration of particles in coal conversion processes and the role of plasticity in liquefaction kinetics.

## Acknowledgements

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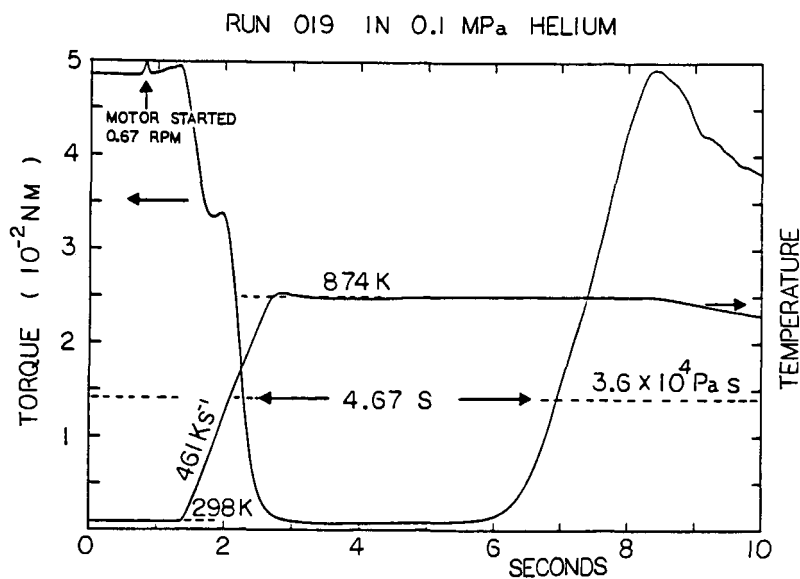


Figure 2 Typical Raw Data from Plastometer. Total Pressure = 0.1 MPa

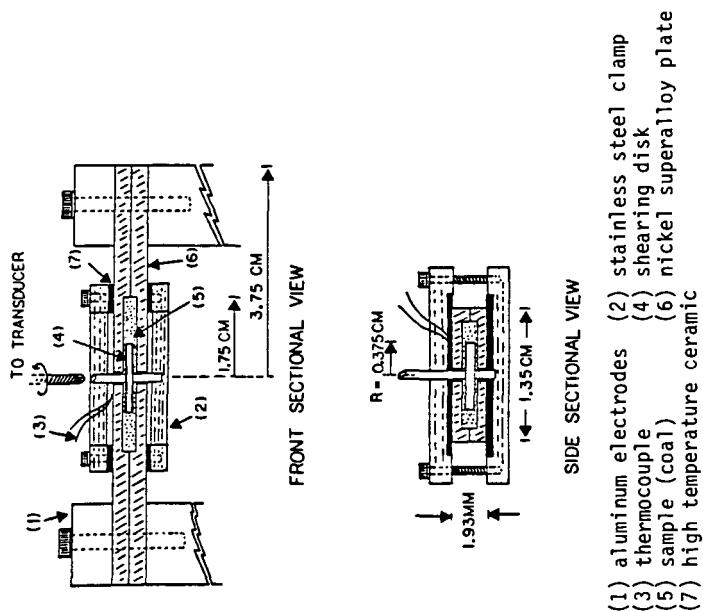


Figure 1 Details of Shearing Chamber

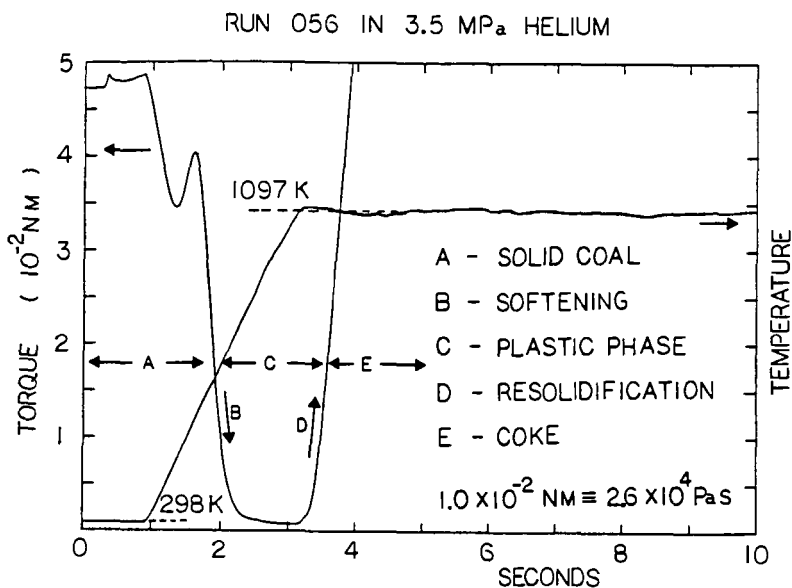


Figure 3 Typical Raw Data from Plastometer. Total Pressure = 3.5 MPa

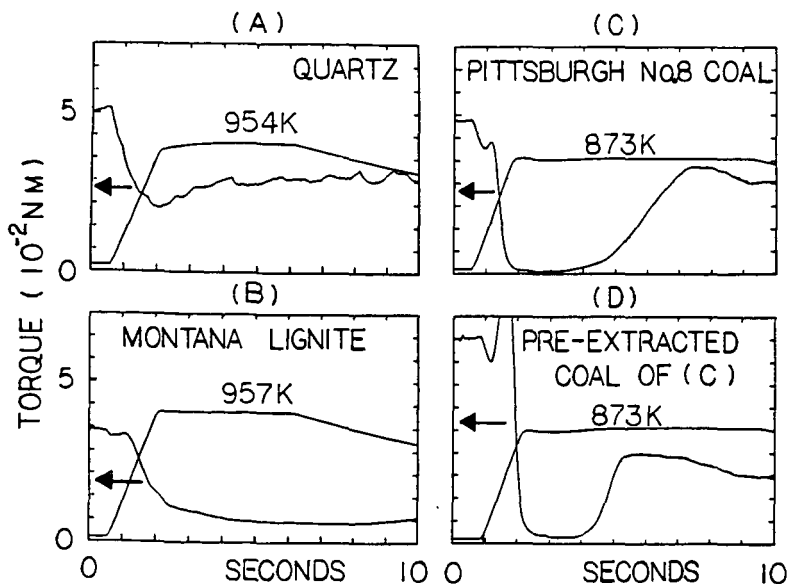


Figure 4 Behavior of Different Particles in the Plastometer



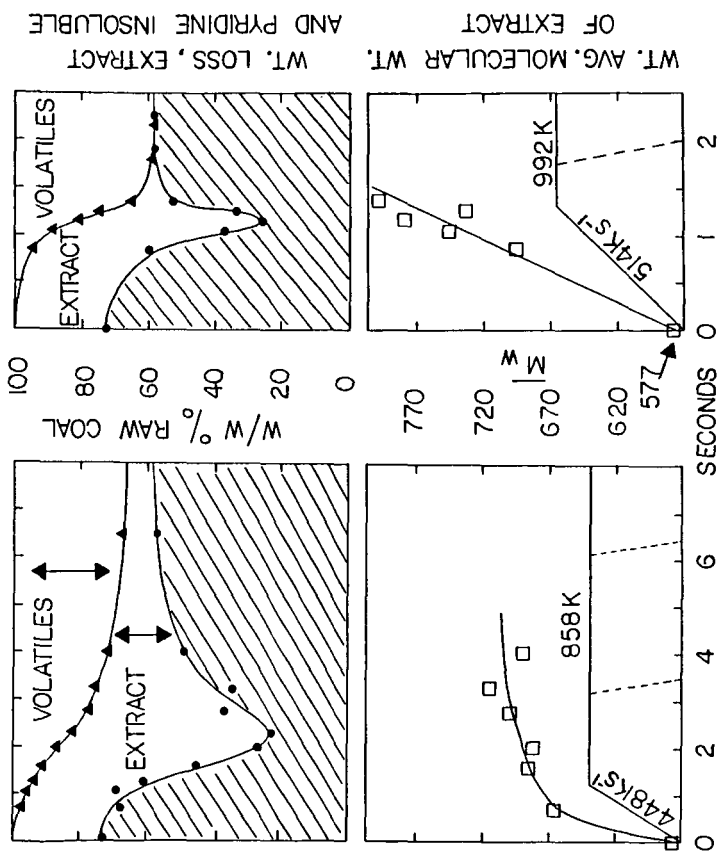


Figure 5  
Figure 6  
Figures 5,6 Weight Loss of Raw Coal, Pyridine Extract and Insoluble from Char and Weight Average Molecular Weight of Extract from Screen Heater Experiments.  
Temperature-time histories indicated.

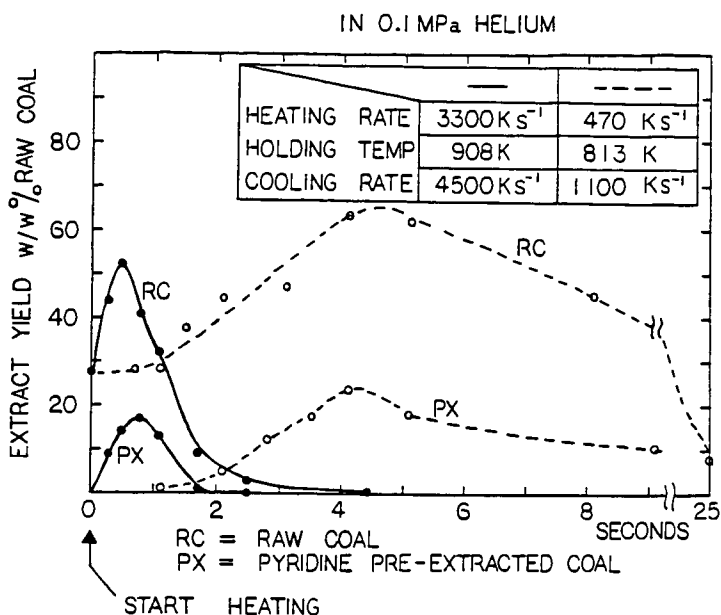


Figure 7 Comparison of Extract Yields for Raw Coal and Pre-extracted Coal

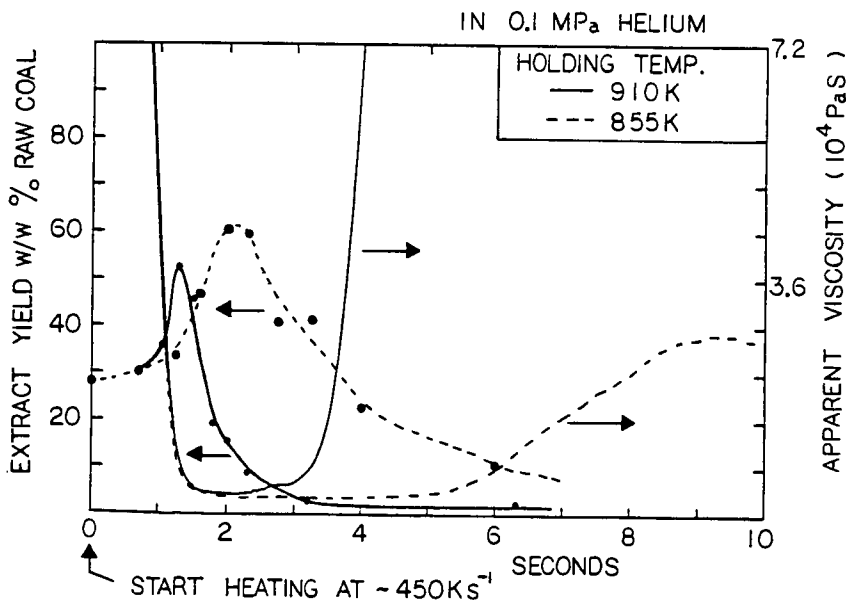


Figure 8 Comparison of Plastic Behavior and Extract Formation/destruction

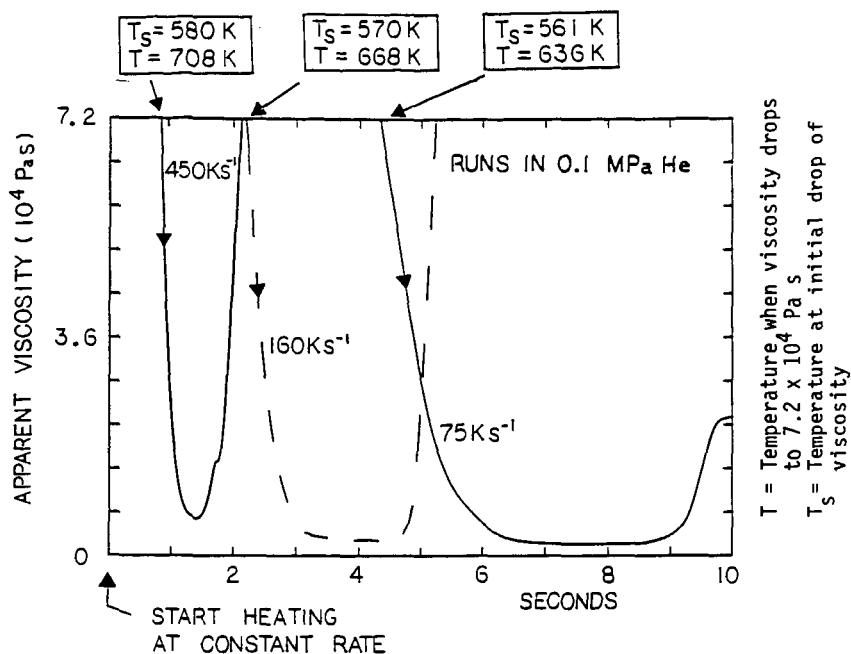


Figure 9 Plasticity Data for Constant Heating Rate Runs

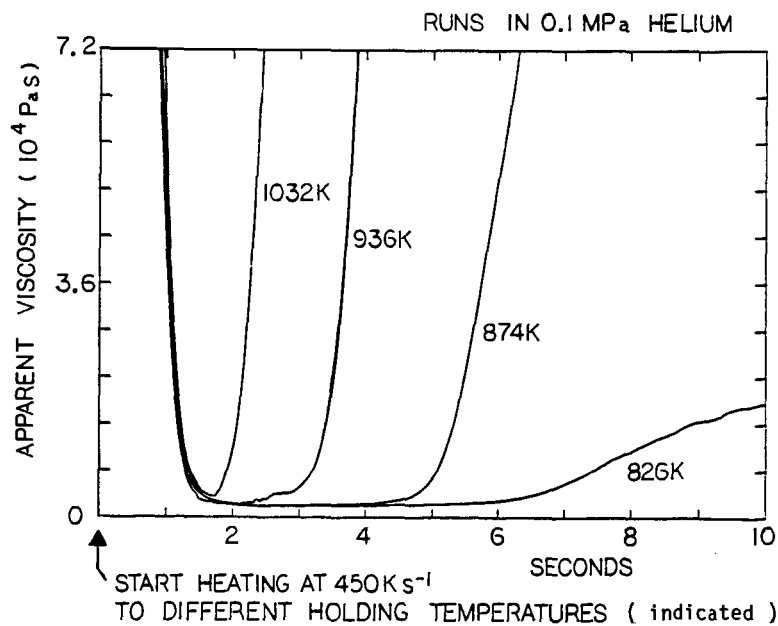


Figure 10 Plasticity Data for Holding Temperature Runs

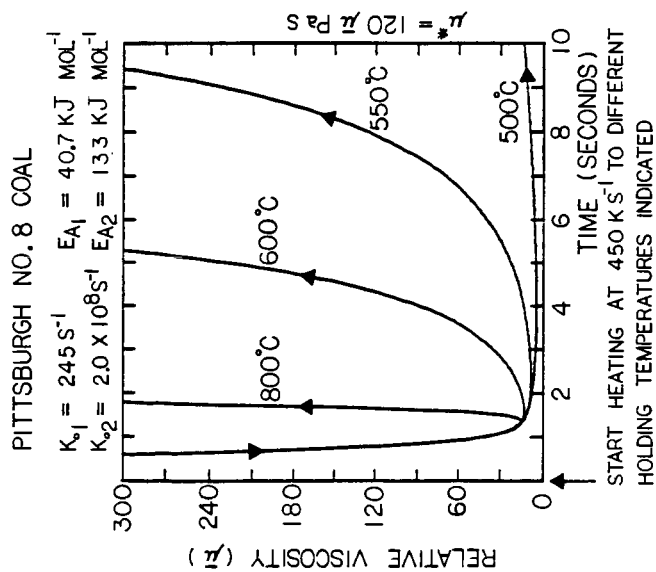


Figure 11 Calculated Viscosity Curve according to Single First Order Reaction Model

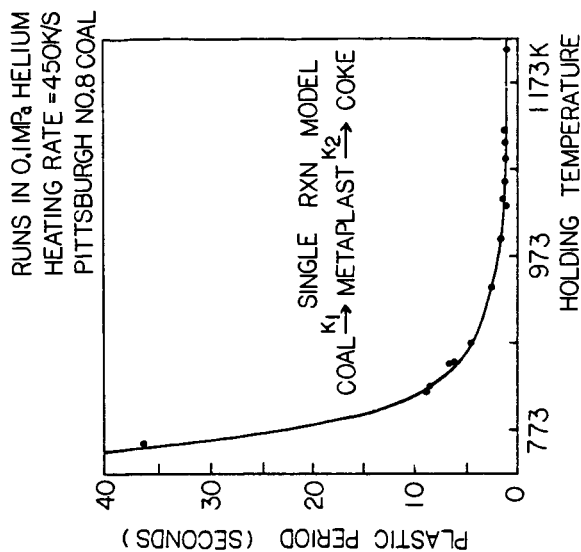


Figure 12 Calculated Plastic Period (curve) and experimental data (solid circles)